Solid State ^{13}C NMR Studies of Coal Char Structure Evolution

M.S. Solum, R.J. Pugmire, D.M. Grant, T.H. Fletcher, and P. Solomon

University of Utah
Salt Lake City, Utah 84112

Combustion Research Facility
Sandia Livermore National Laboratory
Livermore, California 94550

and
Advanced Fuel Research
Hartford, Connecticut 06108

ABSTRACT

Solid state ^{13}C NMR techniques have been used to study the evolution of char structure during pyrolysis processes. The effects of residence time, heating rate, and final char temperature are observed. The NMR data demonstrates that extensive loss of aromatic ring bridge material precedes significant change in aromatic cluster size.

I. Introduction

All coal conversion processes are controlled by thermal decomposition in which the coal is transformed into volatiles and char. To study this process, investigators have focused on how various parameters change with the extent of decomposition (such as weight loss, volatile evolution, functional group composition, reactivity, solvent swelling ratio, tar molecular weight distribution, extract yields, etc.) In this study a series of chars for which weight loss and volatile evolution data has been previously obtained has been subjected to a variety of measurements to characterize the coal to char transformation. This report focuses on ^{13}C solid state NMR spectroscopy to obtain functional group composition and other structure data. A subsequent paper will present characteristics of the same chars obtained by ^{13}C NMR, FT-IR, solvent swelling, and oxygen reactivity[1]. The identification of the chemistry of the coal to char transformation is particularly important to the development of network models for coal thermal decomposition (1,2).

In the past decade ^{13}C solid state NMR spectroscopy, because of its nondestructive nature and unique capabilities, has been used in the structural analysis of solid fossil fuel samples.[3,4] Using cross-polarization[5-9] (CP), magic angle spinning[7,10-12] (MAS), and dipolar decoupling techniques[12,13] a direct measurement of the relative number of aromatic and non-aromatic carbons is possible.[14] The aromaticity, f_a', has been reported for whole coals, macerals, soil and other fossil fuel related materials.[14-19] Other researchers have also used dipolar dephasing (DD) techniques [20-22] along with normal CP/MAS integrations over selected chemical shift ranges to subdivide f_a' values into the amount of protonated and nonprotonated carbon[23-27] These techniques have recently been used to estimate the average aromatic cluster size of the eight coals in the Argonne Premium Coal Sample Bank (APCSB).[28] In more sophisticated experiments, the analysis of chemical shielding tensor

components has been used to estimate the cluster size of anthracite coals and a fusinite coal maceral.[29]

We have recently turned our attention to the study of coal chars in order to assess the changes in the carbon skeletal structure of the char as compared to the parent coal. The char cluster size has been of particular interest as part of our long range goal of understanding the relationship between char structure and reactivity. We have recently begun a study of a series of chars produced from different coals at different heating rates and final temperatures.

II. Experimental

A. NMR Experiments

The data on coals and chars were obtained according to the method described by Solum.[28] Relaxation parameters were determined on the parent coal and each char as well as the carbon structural distribution.

B. Char Preparation

Chars for this study were prepared at AFR (Zap and Pitt. #8 coals) by pyrolysis in an inert atmosphere in one of three reactors as discussed in Reference 30. The chars from the Illinois No. 6 coal were prepared in an entrained flow reactor at the Combustion Research Facility at Sandia National Laboratories as described in Reference 31.

III. Results and Discussion

A. Cluster Size Determination

The carbon skeletal structure of the parent coals and related chars are presented in Tables 1-4. The definition of these carbon structural distribution parameters is given by Solum, et. al.[28] As pointed out in the analysis of the APCSB coals, the amount of bridgehead carbon f_a^B present is an important structural parameter. The mole fraction of aromatic bridgehead carbons, χ_b is defined as $\chi_b = f_a^B / f_a'$ where f_a' is the fraction of aromatic carbons present in the sample. This parameter is important as it can be used to estimate the aromatic cluster size (see reference 28).

B. Char Structure Analysis

The data in Tables 1-4 represent a variety of experimental conditions on different coals. The data on the Zap coals were obtained by both rapid and slow heating techniques on two different coal samples. For the slow heating case, the chars were produced by heating an APCSB Zap coal at 0.5 deg/sec with a 3 minute hold at the final temperature. The rapid heating Zap, Illinois #6, and Pittsburgh #8 data were taken at heating rates of ~10^4 deg/sec at various temperatures and residence times. The Illinois #6 data was obtained from a set of char samples produced from a 106-125 μ coal. The reactor residence times were 50 ms and 105 ms with sample temperatures measured at 850 and 1100°K, respectively for the two samples.

At this stage of the work, it appears that four structural parameters are informative. In Figure 1, the relationship between aromaticity and cluster size is apparent for the Pitt. #8 coal and related chars. Only char data from Table 3 for similar residence times are included in the plot. It is apparent from the remainder of the data on Pitt. #8 (and the Illinois #6 data) that

residence time at a given temperature is an important consideration. However, sufficient data is not available at the present time to permit a detailed assessment of this effect although the general trend is obvious from the data. While the aromaticity changes with temperature, it is clear that the cluster size has not changed at 973°K. At 1073°K, one observes the onset of cluster growth (but not at the shorter residence time, i.e., 1073°K/12″ in Table 1) by a factor of 25% while at 1373°K the cluster size has doubled. In Figure 2 the percent of aliphatic carbon is compared to the aromatic attachment sites/100 carbons. As the pyrolysis temperature increases a significant reduction is noted in the aliphatic carbon content. However, the number of attachment sites (alkyl and alkoxyl functional groups) on aromatic carbons exhibits essentially no change. Similar effects are noted in Figures 3 and 4 for the rapid and slow heating conditions for Zap lignite.

The data on PSOC-1493 represents only two samples from the pyrolysis series. While the aromaticity has started to increase at 1100°K (105 ms residence time) the aromatic cluster size has not changed (Figure 5). However, the decrease in aliphatic carbon content together with little or no change in the number of aromatic attachment sites per 100 carbon atoms is similar to the other char data.

The four sets of char data demonstrate a consistent pattern. As the temperature and/or residence time for pyrolysis increases, one observes an increase in aromaticity of the char (relative to the parent coal) and a concomitant decrease in the amount of aliphatic carbon remaining in the char. The average aromatic cluster size does not change in the 850-1100°K temperature range for the two high volatile bituminous coals studied and only increases significantly above ~ 1100°K. In the case of the Zap coals, the slow heating data displays a monotonic relationship between cluster size and final temperature. In the rapid heating case, the effects of residence time on cluster size is clearly evident. Whether this effect is due to the fact that the temperatures are in excess of 1000°K (1073 and 1873) or to the nature of the coal is not clear from this limited data set.

The other significant phenomena are the decrease in aliphatic carbon content with essentially no variation in the number of aromatic bridge and side chain attachment sites. These data are consistent with models[1,2] for coal devolatilization wherein tar production is accompanied by expulsion of bridge material and stabilization of dangling free radicals by hydrogen transfer reactions or expulsion as light gases. Hence, the data suggest that the evolution of char structure is a function of heating rate, final temperature, and residence time. During pyrolysis, aliphatic rich material is preferentially expelled as tar and light gases. In the initial stages of pyrolysis, it appears that there is no onset of aromatic cluster size growth until the temperature approaches 1100°K in the fast heating regime, i.e., ~ 10^4/sec. The loss of aliphatic carbon appears to be through expulsion of bridge material which leaves a host of short side chains and bridges still intact. The details of this mechanism are being evaluated and we will supplement these preliminary char studies with a more extensive set of data[30] and a set of carefully prepared char/tar pairs.

Acknowledgements

This work was supported by the National Science Foundation under Cooperative Agreement No. CDR 8522618. Also participating in the funding of this effort in alphabetical order, were a consortium of organizations that include: Advanced Fuel Research Inc.; Allison Division (General Motors Corp.); Babcock and Wilcox; Chevron Research Co.; Combustion Engineering, Inc.; Conoco, Inc.; Convex Computer Corp.; Corning Glass Works; Dow Chemical USA; Electric Power Research Institute; Empire State Electric Energy Research Corp.; Foster Wheeler Development Corp.; Gas Research Institute; General Electric Co.; Los Alamos National Laboratory; Morgantown Energy Technology Center (U.S. Dept. of

Energy); Pittsburgh Energy Technology Center (U.S. Dept. of Energy); Pyropower Corp.; Questar Development Corp.; Shell Development Co.; Southern California Edison; the State of Utah; Tennessee Valley Authority; and Utah Power and Light Co. Brigham Young University and the University of Utah financial support is also acknowledged. Additional support (for Advanced Fuels Research) was provided by the DOE through the Morgantown Energy Technology Center (for AFR, Contract DEAC21-86MC23075) and the Pittsburgh Energy Technology Center (for CRF and through the Consortium for Fossil Fuel Liquefaction Science for the University of Utah).

References

1. Solomon, P.R.; Hamblen, D.G.; Carongelo, R.M.; Serio, M.A.; and Desphande, G.V. Energy & Fuels, 1988 2, 405.

2. Grant, D.M.; Pugmire, R.J.; Fletcher, T.H.; and Kerstein, A.R. Energy & Fuels, 1989, 8, (in press).

3. Axelson, D.E. Solid State Nuclear Magnetic Resonance of Fossil Fuels; Multi Science: Canada, 1985.

4. Davidson, R.M. Nuclear Magnetic Resonance Studies of Coal; IEA Coal Research: London, 1986.

5. Hartmann, S.R.; Hahn, E.L. Phys. Rev., 1962, 128, 2042.

6. Pines, A.; Gibby, M.G.; Waugh, J.S. J. Chem. Phys., 1972, 56, 1776.

7. Mehring, M. In High Resolution NMR Spectroscopy in Solids; Diehl, P.; Fluck, E.; Kosfeld, R., Eds.; NMR-Basic Principles and Progress; Springer Verlag: New York 1976; Vol 11.

8. Alemany, L.B.; Grant, D.M.; Pugmire, R.J.; Alger, T.D.; Zilm, K.W. J. Am. Chem. Soc., 1983, 105, 2133.

9. Alemany, L.B.; Grant, D.M.; Pugmire, R.J.; Alger, T.D.; Zilm, K.W. J. Am. Chem. Soc., 1983, 105, 2142.

10. Andrew, E.R.; Bradbury, A.; Eades, R.G. Nature, 1959, 183, 1802.

11. Lowe, I.J. Phys. Rev. Lett., 1959, 2, 285.

12. Schaefer, J.; Stejskal, E.O.; Buchdahl, R. Macromolecules, 1975, 8, 291.

13. Pines, A.; Gibby, M.G.; Waugh, J.S. J. Chem. Phys., 1973, 59, 569.

14. VanderHart, D.L.; Retcofsky, H.L. Fuel, 1976, 55, 202.

15. Botto, R.E.; Wilson, R.; Winans, R.E. Energy & Fuel, 1987, 1, 173.

16. Sullivan, J.J.; Maciel, G.E. Anal. Chem., 1982, 54, 1615.

17. Vassallo, A.M.; Wilson, M.A.; Collin, P.; Oades, J.M.; Waters, A.G.; Malcolm, R.L. anal. Chem., 1987, 59, 558.

18. Hagaman, E.W.; Chambers, R.R.; Woody, M.C. Anal. Chem., 1986, 58, 387.

19. Vassallo, A.M.; Wilson, M.A.; Edwards, J.H. Fuel, 1987, 66, 622.

20. Alla, M.; Lippmaa, E. Chem. Phys. Lett., 1976, 37, 260.

21. Opella, S.J.; Frey, M.H. J. Am. Chem. Soc., 1979, 101, 5854.

22. Alemany, L.B., Grant, D.M., Alger, T.D.; Pugmire, R.J. J. Am. chem. Soc., 1983, 105, 6697.

23. Alemany, L.B.; Grant, D.M.; Pugmire, R.J.; Stock, L.M. Fuel, 1984, 63, 513.

24. Wilson, M.A.; Collin, P.J.; Pugmire, R.J.; Grant, D.M. Fuel, 1982, 61, 959.

25. Wilson, M.A.; Pugmire, R.J.; Karas, J.; alemany, L.B.; Woolfenden, W.R.; Grant, D.M.; Given, P.H. Anal. Chem., 1984, 56, 933.

26. Soderquist, A.; Burton, D.J.; Pugmire, R.J.; Beeler, A.J.; Grant, D.M.; Durand, B.; Huk, A.Y. Energy & Fuels, 1987, 1, 50.

27. Derenne, S.; Largeau, C.; Casadervall, E.; Laupretre, F. Fuel, 1987, 66, 1086.

28. Solum, M.S.; Pugmire, R.J.; and Grant, D.M. Energy & Fuels, 1989, 3, in press.

29. Sethi, N.K.; Pugmire, R.J.; and Grant, D.M. Anal. Chem., 1988, 60, 1574.

30. Solum, M.S.; Pugmire, R.J.; Grant, D.M.; Fletcher, T.H.; and Solomon, P.R. solid State ^{13}C NMR Studies of Coal Char Structure Evolution: I. Submitted.

31. Fletcher, T.H. Time-Resolved Temperature Measurements of Individual Coal Particles During Devolatilizaiton Sandia Report , SAND88-8635, September, 1988.

TABLE 1. Carbon Structural Parameters for Chars Produced from A Zap Coal Under Rapid Heating (10^4 deg/sec) Conditions

MATERIAL	f_a	$f_{a'}$	f_a^C	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
AFR ZAP	.74	.61	.13	.23	.38	.10	.19	.09	.26	.15	.11	.07
CHAR 800°C (0.5 m)	.75	.63	.12	.21	.42	.10	.17	.15	.25	.12	.13	.07
CHAR 800°C (2.4 m)	.87	.83	.04	.35	.48	.06	.19	.23	.13	.--	.--	.07
CHAR 1600°C (60 ms)	.83	.77	.06	.38	.39	.06	.18	.15	.17	.--	.--	.10
CHAR 1600°C (160 ms)	.88	.84	.04	.26	.58	.06	.22	.30	.12	.--	.--	.07

MATERIAL	χ_b	CARBONS PER CLUSTER
AFR ZAP	0.148	8.5
CHAR 800°C 0.5 m	0.238	11.4
CHAR 800°C 2.4 m	0.277	13.3
CHAR 1600°C 0"	0.195	9.8
CHAR 1600°C 4"	0.357	17.8

TABLE 2. Carbon Structural Parameters for Chars Produced from Argonne PCSB Zap Coal. Hold Time at Final Temperature was 3 Minutes.

MATERIAL	f_a	$f_{a'}$	f_a^C	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
ZAP COAL	.61	.54	.07	.26	.28	.06	.13	.09	.39	.25	.14	.12
CHAR 200°C (3 min)	.72	.62	.10	.24	.38	.08	.17	.13	.28	.21	.07	.08
CHAR 300°C (3 min)	.77	.69	.08	.28	.41	.08	.18	.15	.23	.--	.--	.06
CHAR 400°C (3 min)	.79	.72	.07	.27	.45	.08	.19	.18	.21	.--	.--	.07
CHAR 500°C (3 min)	.86	.79	.07	.29	.50	.10	.17	.23	.14	.--	.--	.06

MATERIAL	χ_b	CARBONS PER CLUSTER
ZAP COAL	0.167	9.0
CHAR 200°C (3 min)	0.210	10.4
CHAR 300°C (3 min)	0.217	10.6
CHAR 400°C (3 min)	0.250	12.0
CHAR 500°C (3 min)	0.291	14.1

TABLE 3. Carbon Structural Parameters for Pittsburgh #8 Coal and Chars Produced at Different Temperatures and Residence Times

MATERIAL	f_a	$f_{a'}$	f_a^C	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
PITTSBURGH #8	.71	.67	.04	.28	.39	.09	.16	.14	.29	.17	.12	.07
CHAR 700°C 24"	.80	.75	.05	.34	.41	.08	.19	.14	.20	.10	.10	.08
CHAR 800°C 12"	.76	.71	.05	.29	.42	.08	.20	.14	.24	.12	.12	.08
CHAR 800°C 24"	.80	.77	.03	.35	.42	.06	.16	.20	.20	.10	.10	.08
CHAR 1100°C 20"	.88	.85	.03	.33	.52	.04	.16	.32	.12	.--	.--	.06
CHAR 1100°C 24"	.89	.85	.04	.27	.58	.04	.21	.33	.11	.--	.--	.06

MATERIAL	χ_b	CARBONS PER CLUSTER
PITTSBURGH #8	0.209	10.3
CHAR 700°C 24"	0.187	9.6
CHAR 800°C 12"	0.197	9.9
CHAR 800°C 24"	0.260	12.5
CHAR 1100°C 20"	0.376	18.6
CHAR 1100°C 24"	0.388	19.2

TABLE 4. Carbon Structural Parameters for Chars Produced from an Illinois No. 6 Coal

MATERIAL	f_a	$f_{a'}$	f_a^C	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
PSOC-1493 COAL	.71	.67	.04	.27	.40	.08	.17	.15	.29	.15	.14	.07
CHAR 1250 K 40 mm	.72	.67	.05	.29	.38	.09	.19	.10	.28	.18	.10	.07
CHAR 1250 K 100 mm	.79	.74	.05	.34	.40	.07	.19	.14	.21	.--	.--	.08

MATERIAL	χ_b	C	$\sigma + 1$
PSOC-1493	0.224	10.8	4.0
CHAR 1250 K 40 mm	0.149	9.6	4.0
CHAR 1250 K 100 mm	0.189	9.7	3.4

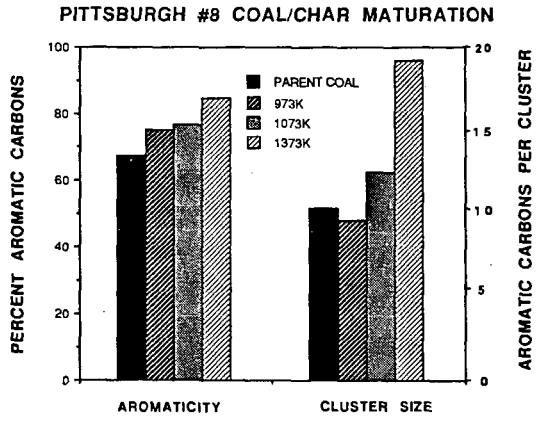

Figure 1. Relationship between aromaticity and cluster size for a Pitt. #8 coal and related chars.

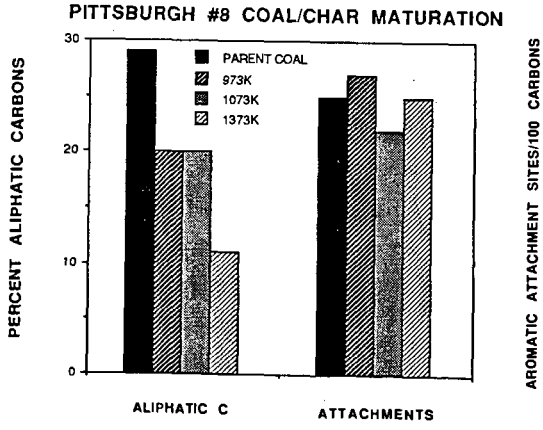

Figure 2. Relationship between aliphatic carbon content and number of aromatic attachment sites 1100 carbons for a Pitt. #8 coal and related chars.

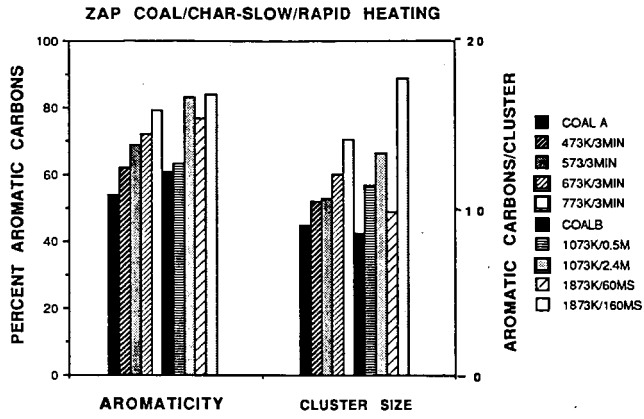

Figure 3. Relationship between aromaticity and cluster size for Zap coals and related chars heated under rapid heating conditions and APCSB Zap coal heated at 0.5 deg/sec with a hold time of 3 minutes.

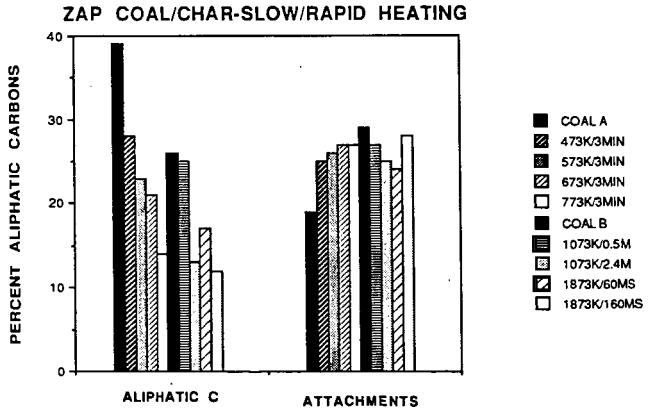

Figure 4. Relationship between aliphatic carbon content and number of aromatic attachment sites/100 carbons for the coals described in Figure 5.

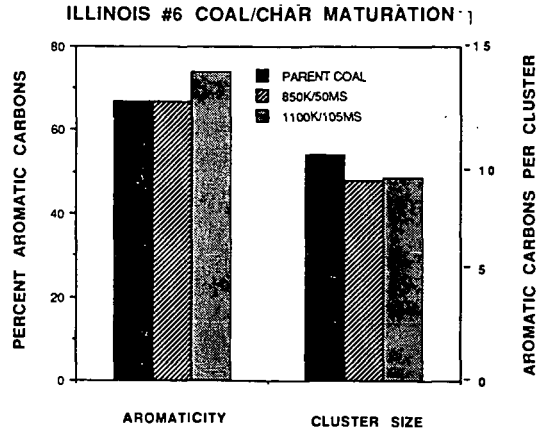

Figure 5. Relationship between the aromaticity and cluster size for an Illinois #6 coal (PSOC-1493) and related chars.

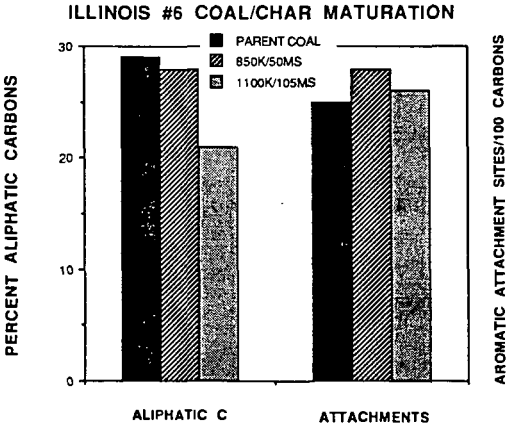

Figure 6. Relationship between aliphatic carbon content and number of aromatic attachment sites/100 carbons for the Illinois #6 coal and associated chars.